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HEINZE GASOMETER METHOD FOR QUANTITATIVE DETERMINATION OF CARBONATES IN TILLS

by

W.C. Ross

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INTRODUCTION

The 'Heinze Gasometer Method' is the designated name for an efficient laboratory procedure which uses the Heinze Gasometer for the quantitative determination of calcite and dolomite and the equivalent total carbonates in unconsolidated sediments.

This is a further extension and application of the method and equipment as described by Christiansen and Ross (1971) and Perkins and Dyck (1973) respectively.

This apparatus, unique in its design, eliminates the variables which are common to traditional gasometers so that the final print–out is a continuous arithmetic curve which expresses the rate of CO_2 evolution. The gas volumes are corrected to standard temperature and pressure (STP).

Each arithmetic curve is converted to semilogarithmic by a manual replot, and the continuous decay curve is transformed to a continuous assemblage of straight–line segments. With simple calculations of specific volume–time values, the weight percentages of calcite and dolomite are determined.

The carbonate results are believed to be absolute. A statistical linear regression evaluation proved the analyses by the Heinze Gasometer method to be comparable to the results determined by the Atomic Absorption Method (Ross 1986).

The coefficients of correlation are as follows:

weight percent calcite – 0.923

weight percent dolomite – 0.983

weight percent total CO_2 – 0.989

The precision of analyses is satisfactory. Results of duplicate analyses may vary slightly but are within acceptable limits for their application in stratigraphic studies.

Error of analyses is attributed to the inhomogeneity of the carbonate distribution within samples and signifies insufficient time of mixing in the procedure for sample preparation.

If the gasometer was to be directly connected to a computer, this operation could increase analytical efficiency by three–fold, and reduce the cost.

An established laboratory which is equipped with a sink, fume hood, etc. may add the gasometer, and complimentary equipment, at a minimum expense.

HEINZE GASOMETER[1]

The Heinze Gasometer is unique in its design. Like other gasometers it accommodates the carbonate–acid reaction and measures the volumes of the evolved CO_2 gas, but unlike contemporary gasometers its 'built–in' features compensate for the variables of temperatures (both reaction and atmospheric), atmospheric pressure, and added acid volumes so that the recorded volumes are at standard temperature and pressure (STP). Furthermore the gasometer appendage, an electronic recorder, produces an arithmetic curve for each analysis, the rate of CO_2 evolution curve, and this continuous curve is the time interval of analysis for the complete reaction, i.e. from the time that the acid is first added to the samples, and continuously and cumulatively records the volumes until the maximum volume is evolved.

The Heinze Gasometer is a durable laboratory apparatus, and an additional advantage of this equipment is that maintenance is minimal, consequently the shut down time is seldom more than one hour in a week of continuous use.

A sketch of the apparatus, together with notations that explain the function of individual components, is illustrated by Figures 1A and 1B. Not included in the sketch are the electric control panel box and the one–point Heath Schlumberger strip recorder, model No. SR204.

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[1] Heinze Gasometer – named after the inventor and manufacturer, Mr. R. Heinze, a former employee (retired) of the Canadian Centre for Advanced Instrumentation, Saskatchewan Research Council.

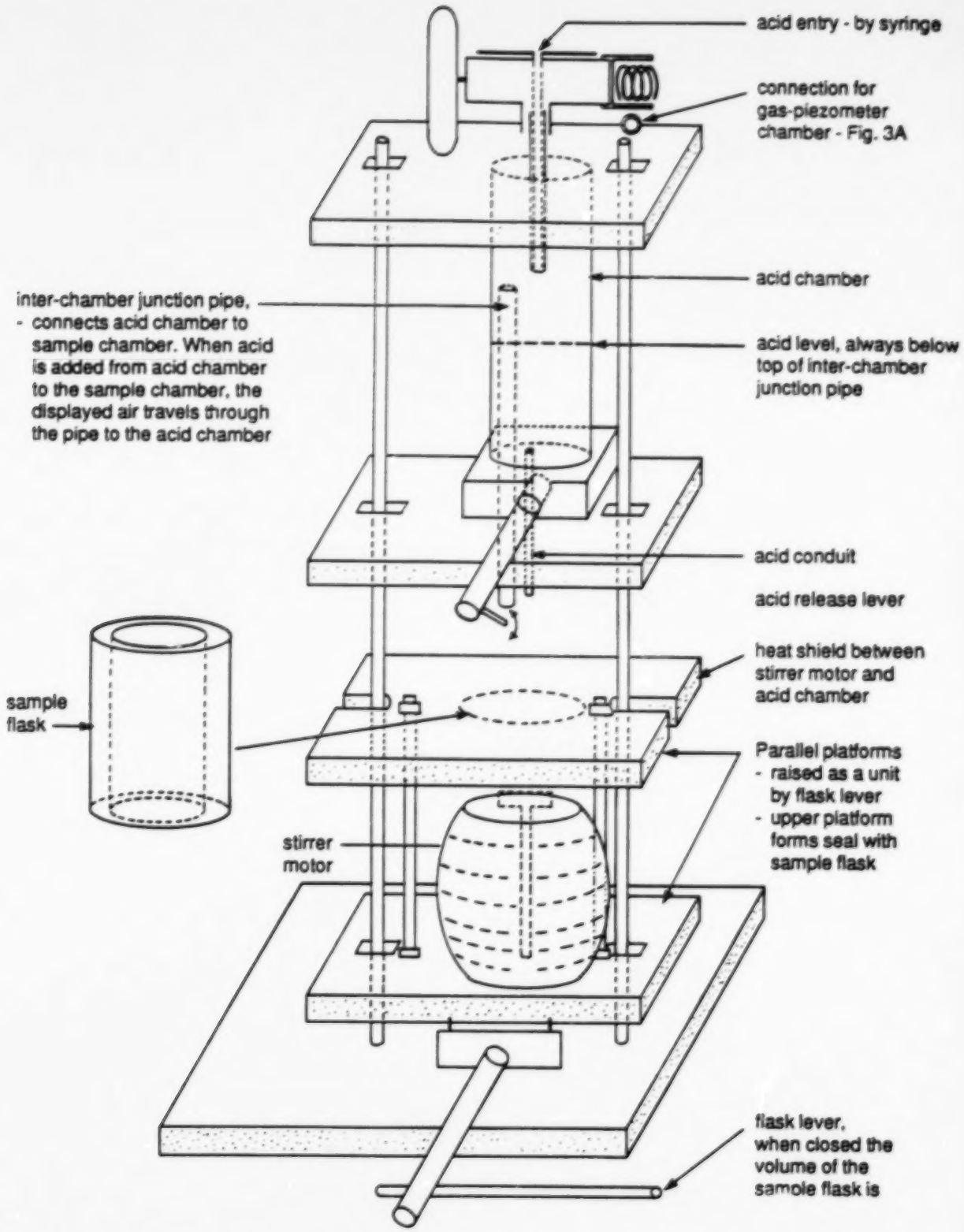
acid entry - by syringe
connection for gas-piezometer chamber - Fig. 3A
acid chamber
inter-chamber junction pipe,
- connects acid chamber to sample chamber. When acid is added from acid chamber to the sample chamber, the displayed air travels through the pipe to the acid chamber
acid level, always below top of inter-chamber junction pipe
acid conduit
acid release lever
heat shield between stirrer motor and acid chamber
sample flask
Parallel platforms
- raised as a unit by flask lever
- upper platform forms seal with sample flask
stirrer motor
flask lever, when closed the volume of the sample flask is

Figure 1A. Sketch of 'Heinze' Gasometer

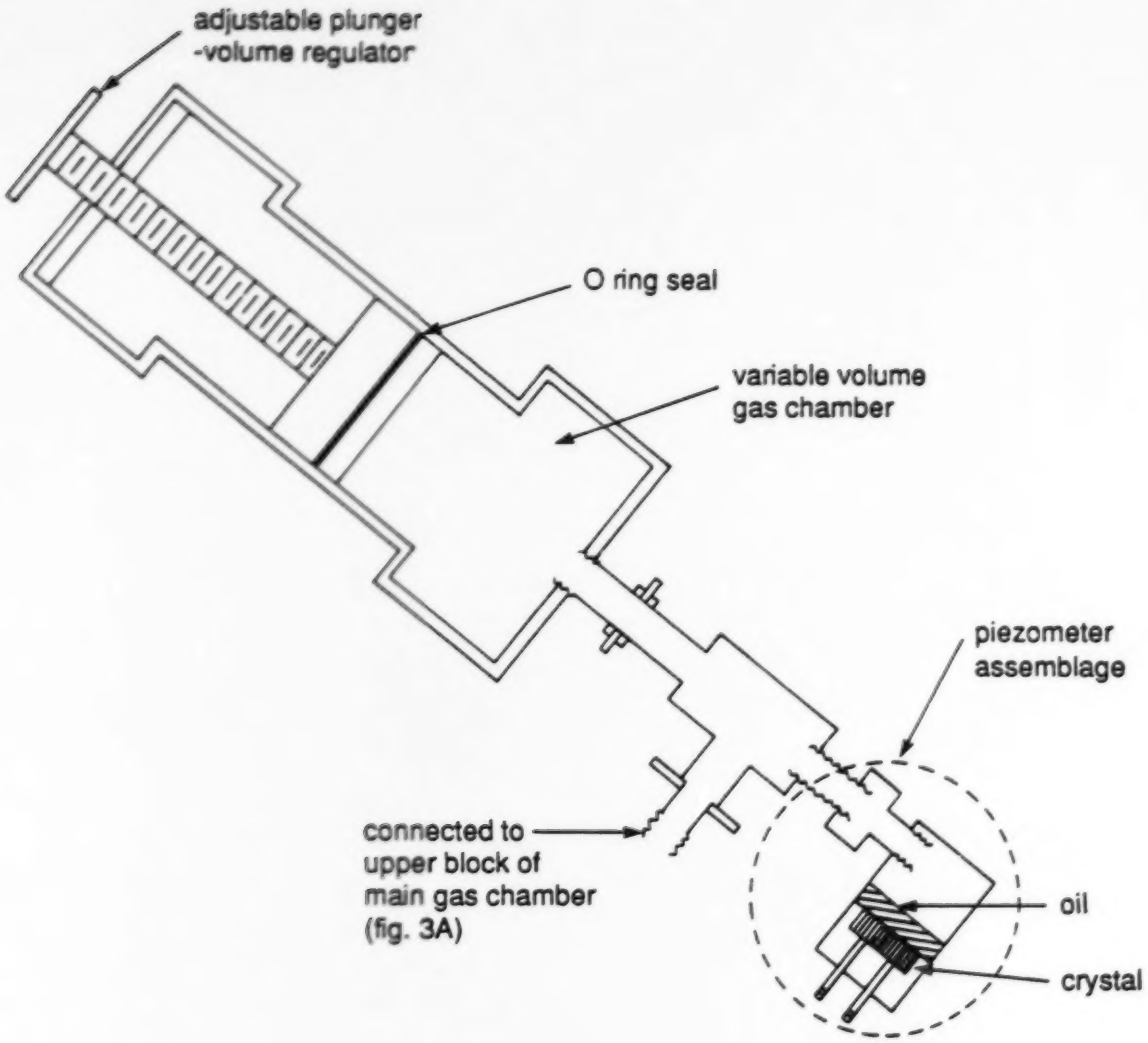

Figure 1B. Adjustable Gas–Piezometer Chamber
Supplement to Figure 3A

THEORETICAL CONSIDERATIONS

Grain Size < 2 mm

Carbonate analyses are restricted to samples of size range less than 2 mm (defined as till matrix). This range is adequate for gasometric analyses when both calcite and dolomite minerals are present in the sample. (This is generally the case for tills in southern Saskatchewan).

Grain Size < 0.0652 mm

The < 2 mm samples are reduced to < 0.0652 mm by machine grinding (a time–size study is required). The < 0.065 mm grain size is preferred for carbonate analyses, because the grinder serves also as a blender, and the samples are more homogeneous, also, erratic sized carbonate grains are reduced. Grain sized samples < 0.0652 mm show better precision of results (duplicate analyses) than the results of the < 2 mm grain size samples.

Rate of CO_2 Evolution

The rate of CO_2 evolution for dolomite is greater than the rate of CO_2 evolution for calcite providing that the grain size of the two carbonates are equal, and factors of acid strength, temperature, et al., are the same for both minerals.

In the grain sizes of mixtures of calcite and dolomite within a sediment, the upper limit of the grains is fixed, either by sieving (< 2 mm) and by grinding (< 0.0625 mm).

The rate of CO_2 evolved by calcite is greater than the rate of CO_2 evolved by dolomite.

The application of this corollary is the basis for determining the evolved CO_2 from dolomite and calcite. This concept will be enlarged upon within the section titled 'Graphic Curves' of this report.

BASIC ASSUMPTIONS

1) Tills in southern Saskatchewan contain the carbonate minerals of calcite and dolomite. Rarely the carbonates may be absent due to excessive weathering. Generally both minerals are present. X–ray diffraction analyses of numerous tills shows that other carbonates are absent, or in such small quantity that they escape detection (< 5% by weight).

2) Gram Molecular Weights (G.M.W.) of Calcite and Dolomite –

   Calcite (G.M.W.) used in calculations = 100.09 gm.

   Dolomite (Formula Weight) used in calculations = 92.206 gm. assuming that Ca:Mg = 1:1

3) Variables that alter gas volumes are controlled by the design of the gasometer.

   (a) Placement of a heat shield between the stirrer motor and the gas collection chamber (sample flask).

   (b) Exothermal heat of reaction is negligible considering the volume of gas collection chamber, sample size, and required time of total reaction.

   (c) Acid vapour pressure is always constant. This is insured by magnetic stirrer bar, the vapour phase is maximum, since the acid strength is a constant, acid volume is a constant and temperature of the system is uniform throughout time interval for analysis.

   (d) Room temperature variation is compensated. Every three hours during, and before continuous analyses, an adjustment is made

– 760 mm Hg) (a 0.30000 gm sample of ACS calcite is analyzed by the gasometer). The recorder pin is adjusted, electronically, to read 67.2 mls (Ideal Gas Law volume).

(e) The atmospheric pressure remains relatively constant throughout the time interval for analyses (5 to 18 minutes). The recorder adjustment for temperature (0°C) also adjusts pressure to STP (760 mm Hg).

4) Other Variables Made Constant

(a) Acid – strength is 1:1 HCl

volume is 20 mls – within volume chamber of gasometer, and it is not added to CO_2 volume.

(b) Sample Weight is 1.0000 gm.

This weight was chosen because the constituents carbonates rarely evolve CO_2 in excess of the chart paper limit of 100 mls.; Also the measured total CO_2 evolved is expressed as 'mls CO_2/gm of sample'.

NOTE: The control of the seven variables makes them constant for each analysis, and the chemical reaction of acid on carbonates reduces the system to two components –

Concentration of carbonates –CO_2 evolved mls/gm.

Weight %'s of calcite + dolomite

Also – Rate of reaction of CO_2 evolved:

Rate of CO_2 evolution (calcite) > Rate of CO_2 evolution (dolomite)

LABORATORY PROCEDURE

Refer to the Appendix for an orderly and complete sequence of laboratory procedures.

The arrangement is in 'laboratory manual' form, and is as follows:

1A – Sample Preparation

1B – Gasometer Adjustments

1C – Laboratory Analyses

1D – Graphic Interpretation from CO_2 Curves

1E – Calculations for Calcite and Dolomite

GRAPHIC CURVES

Graphic curves are used for interpreting CO_2 volumes which are evolved by the carbonate constituents of an analyzed sample, and these gas volumes are converted to weight percentages by simple arithmetic for each carbonate mineral, i.e. calcite and dolomite.

For each gasometric analysis, a continuous curve is printed by the recorder of the gasometer. The resultant continuous curve shows the CO_2 volume–time relationship throughout the entire time interval of analysis. This curve is called the 'rate of CO_2 evolution', and it is traced on an arithmetic grid. It is named the 'arithmetic graph'. Figure 2 is an illustration of an arithmetic graph.

The arithmetic graph is transformed into the 'semilog graph'. This operation is presently done by a manual plot of the arithmetic curve on a semilogarithmic grid. Figure 3 represents the semilog graph; Figure 3 is a replot of Figure 2.

The attained semilog graph serves as the model for the interpretation of specific parameters which enable the quantitative determination of calcite and dolomite.

STRAIGHT–LINE SEGMENTS

Preliminary

The semilog graph, for each carbonate analysis, is the final form which contains the required data for the quantitative determination of calcite and dolomite. Although the plot of this graph contains several straight line segments, the procedure for interpretation remains the same.

It is suggested that the reader refer to the semilog graphs, illustrated by Figures 3A and 3B, in order that clarity of the discussed concepts may be enhanced.

General Form of Segments

The straight lines are extended so that they intersect each other. The first segment, with respect to time, intersects the zero time axis (point A, of Figure 3B), and the last segments parallel the time axis (segment FG, l6, of Figure 3B). Intermediate points of intersection are as follows:

Segments	Intersection
l_1 and l_2	B
l_2 and l_3	C
l_3 and l_4	D
l_4 and l_5	E
l_5 and l_6	F

The rule of slopes of linear segments, is as follows:

slopes – $l_1 > l_2 > l_3 > l_4 > l_5 >$ ——l_{final} (with increase in time)

Segment Slope $\frac{1}{\text{time}}$

Significance of Segments

Each straight–line slope represents a uniform logarithmic function of the rate of CO_2 evolution, and the rate of CO_2 evolution is proportional to the carbonate grain size. This implies that each segment not only represents a uniform CO_2 evolution, but also a gradational increase in the grain sizes of the carbonates. It must be emphasized that within each segment the gradational grain size for calcite may differ from the gradational grain size of dolomite, however the evolved CO_2 from each carbonate constituent is additive and does produce a uniform rate of CO_2 evolution.

PARAMETERS

Graphic Interpretation

Follow general rules to pick the graph parameters, as follows:

V_t – total volume of evolved CO_2 (from calcite and dolomite)

The last straight–line segment parallels time axis. Read this volume and record – (unit is mls.).

With reference to Figure 3B, this is at point F, V_t = 37.0 mls.

t_t – time that V_t is reached. This is also total time of reaction.

With reference to Figure 3B, this is at point F, the intersection of segments l_5 and l_6.

It is the time at the intersection of the last two straight line segments. Read and record in minutes.

V_f – total volume of CO_2 evolved from calcite.

Read volume at intersection of second and third last segments. The second last segment is the rate of CO_2 evolution from dolomite only, based on rule – rate of CO_2 evolution from calcite is greater than the rate of CO_2 evolution from dolomite.

With reference to Figure 3B, segment l_5 is CO_2 from dolomite only. V_f is at point E, the intersection of segments l_4 and l_5. V_f = 33.8 mls. Read this volume and record.

t_f – This is the time of completion for total CO_2 evolution from calcite.

It is the time at the intersection of the second and third last segment.

With reference to Figure 3B it is intersection of l_4 and l_5. V_f = 5.8 minutes. Read and record.

V_o – is the apparent volume at time of zero minutes.

It is the intersection of the first segment with the volume axis at time zero minutes.

With reference to Figure 3B, it is the volume by the intercept of segment l_1 with the volume axis. V_o = 3.2 mls. Read and record.

Calculated Parameters:

D_c – is volume of CO_2 from dolomite which is evolved with total calcite CO_2.

$D_c = V_1 \times \frac{t_1}{\overline{t_1}}$ mls; calculate and record in record sheet, Figure 4.

V_c – is the total CO_2 evolved by calcite.

$$V_c = \frac{V_1 + V_o - D_c}{2} \text{ mls}$$

V_d – is total CO_2 evolved by dolomite.

$V_d = V_1 - V_c$ mls

The weight percentage of each carbonate mineral, calcite and dolomite, is calculated by using stoichiometric relationships of the chemical reaction of HCl with the respective mineral.

Calculations are, as follows:

Calcite

$$\text{Wt \% Calcite} = \frac{\text{Volume of Calcite (STP)} \times \text{Gram Equiv. Wt. } CaCO_3 \times 100}{\text{m.w. } CO_2 \times 1.00}$$

Wt % Calcite = $V_c \times 0.44683$

Dolomite

$$\text{Wt\% dolomite} = \frac{\text{Volume of Dolomite (STP)} \times \text{Gram Eq.Alt. } CaMg(CO_3)_2 \times 100}{\text{m.w. } CO_2 \times 100}$$

(assumption – Ca:Mg = 1:1)

Wt % dolomite = $V_d \times 0.41163$

NOTE: Both the graphic and calculated parameters are recorded in an orderly fashion for future reference, Figure 4 is an analytical data sheet which is used by the laboratory for permanent records.

RESULTS

Accuracy

The results of carbonate analyses by the Atomic Absorption Spectrophotometer Method[2] are considered to be absolute values, and consequently this method is used as a standard for comparison of the results obtained by the Heinze Gasometer Method; samples were halved, and each half was analyzed by each method (Ross 1986).

A statistical appraisal by linear regression indicates that both methods, Atomic Absorption and the Heinze Gasometer Method, yield comparable results. The results of the regression are illustrated by Figures 5, 6 and 7.

With a limited number of analyses, 32 duplicate samples, the coefficient of correlations, are as follows:

Wt % Calcite – coeff. of correlation (r) = 0.923

Wt % Dolomite – coeff. of correlation (r) = 0.983

Total CO_2 evolved – coeff. of correlation (r) = 0.989

Precision

On the basis of a limited number of analyses for a sample split, the precision was determined to be as follows:

Calcite – standard deviation 0.30

Dolomite – standard deviation – 0.43

CO_2 evolved – standard deviation – 1.16

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[2] Atomic Absorption Spectrophotometer Method – this procedure is described in another report.

ERRORS

Analytical results of the Atomic Absorption Method are assumed to be absolute values.

Deviation of results by the Heinze Gasometer Method are attributed to one or more factors.

These potential sources of error are as follows:

(1) Inhomogeinity of carbonates in sample due to insufficient mixing. The grinding method used for sample reduction <0.065 mm should mix the carbonates sufficiently.

(2) Large grains of calcite in the < 2 mm fraction may result in the rate of CO_2 evolution from calcite being less than the rate of CO_2 evolution from dolomite, theoretically, with equisize grains of calcite and dolomite, the rate of CO_2 evolution from calcite is greater than that from dolomite.

To overcome this phenomenum the sample should be reduced by mechanical grinding.

(3) Theoretical assumption of CO_2 evolved by dolomite with calcite CO_2 may be incorrect for some analyses. The calculation of this variable (D_c) assumes that the CO_2 from dolomite is evolved at a uniform rate.

The deviation of the determined values is slight, and well within the acceptable limits for the application of carbonate results that are applied to stratigraphic studies.

CONCLUSIONS

The carbonate results by the Heinze Gasometer Method are used to support correlation, and for differentiation of till units in section. The Heinze Gasometer Method for the quantitative determination of carbonates has proved successful for the stratigraphic studies.

In a 600 ft. testhole the total thickness of the till units seldom exceed 300 feet, and with till samples taken every five feet, the number of analysis per testhole is approximately sixty analysis.

The cost of analyses is about $15 per sample. This total includes overhead expenses, laboratory material and depreciation of all equipment. The total cost of carbonate analyses per testhole (with 300 feet of till) is about $900. This total parallels the cost of E–logging the 300 feet.

A standard laboratory is equipped with the necessary facilities (sink, fumehood, etc.) to which may be added the Heinze Gasometer apparatus for an additional cost of about $5000.

Reference was made to the Atomic Absorption Method of carbonate analyses. The precision is excellent, productivity good, but operations such as sample digestion are more involved. The initial cost of the spectrophotometer approaches $30,000. The extra laboratory space required, plus equipment depreciation adds to the cost.

The Heinze Gasometer is a rugged, compact unit with the advantage of portability to temporary field quarters.

Future improvements to the Heinze Gasometer apparatus is a direct linkage to an adequate computer. The recorder that is presently used would be bypassed so that the semilog graph printout would be automatic.

An estimate of potential production increase is approximately three–fold.

REFERENCES

Christiansen, E.A., and Ross, W.C., 1971. Carbonate analysis of tills using a continuously recording gasometer. Saskatchewan Research Council Circular 5–G71–5, 12p.

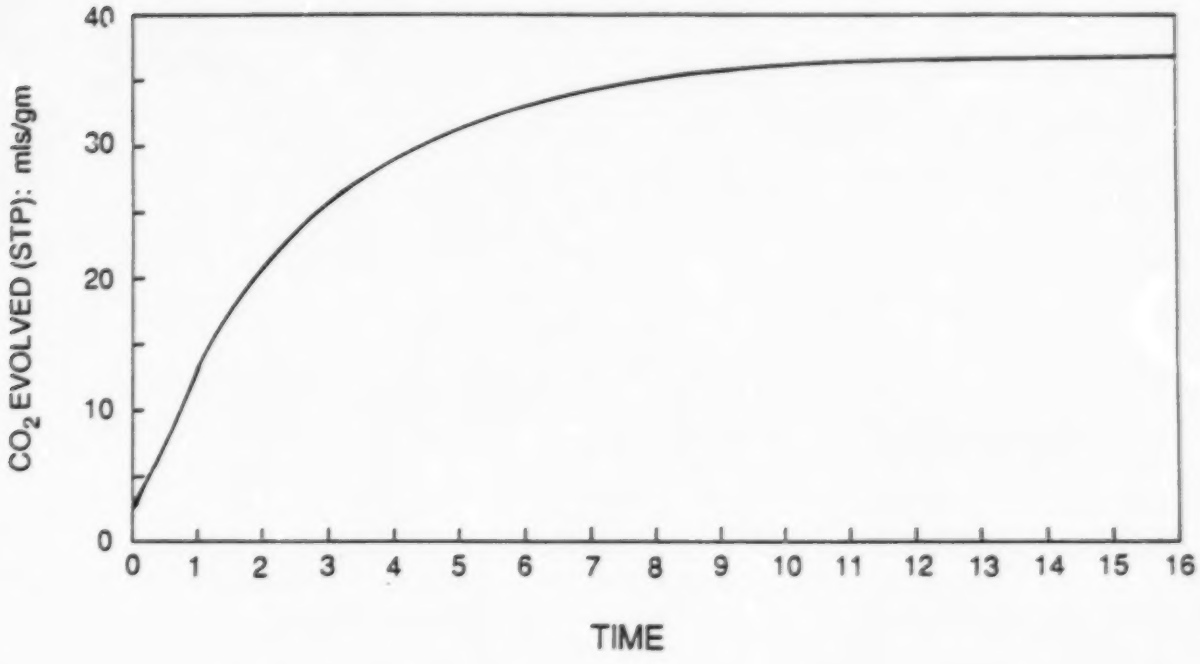
Perkins, E.H., and Dyck, J.H., 1973. Heinze Gas–Volugraph. Saskatchewan Research Council Report p. 73–6, 89p.

Ross, W.C., 1986. Atomic Absorption Method for quantitative determination of carbonates in Tills. Saskatchewan Research Council Technical Report No. 214, 14 p.

SAMPLE NAME - DALMENY SE1-13

depth 50 ft (<2mm GS)

Till Sampie (Rotary Cuttings)



NOTE : Grain Size less than 2.00 mm (Obtained By Seiving)

Figure 2. Arithmetic Graph 'Print–Out' from Recorder of Heinze Gasometer

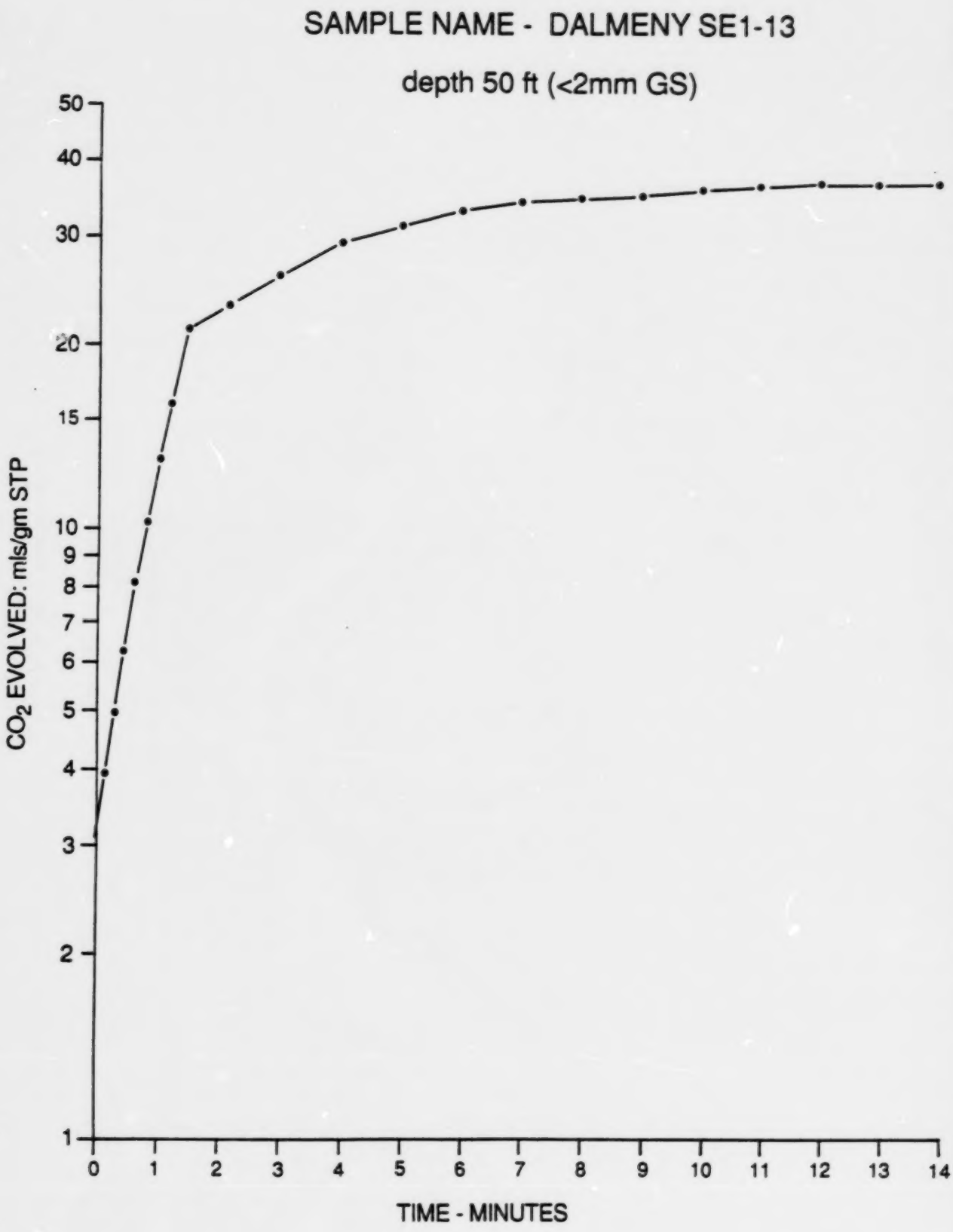


Figure 3A. Semi–Log Graph: Manual Plot from Arithmetic Graph

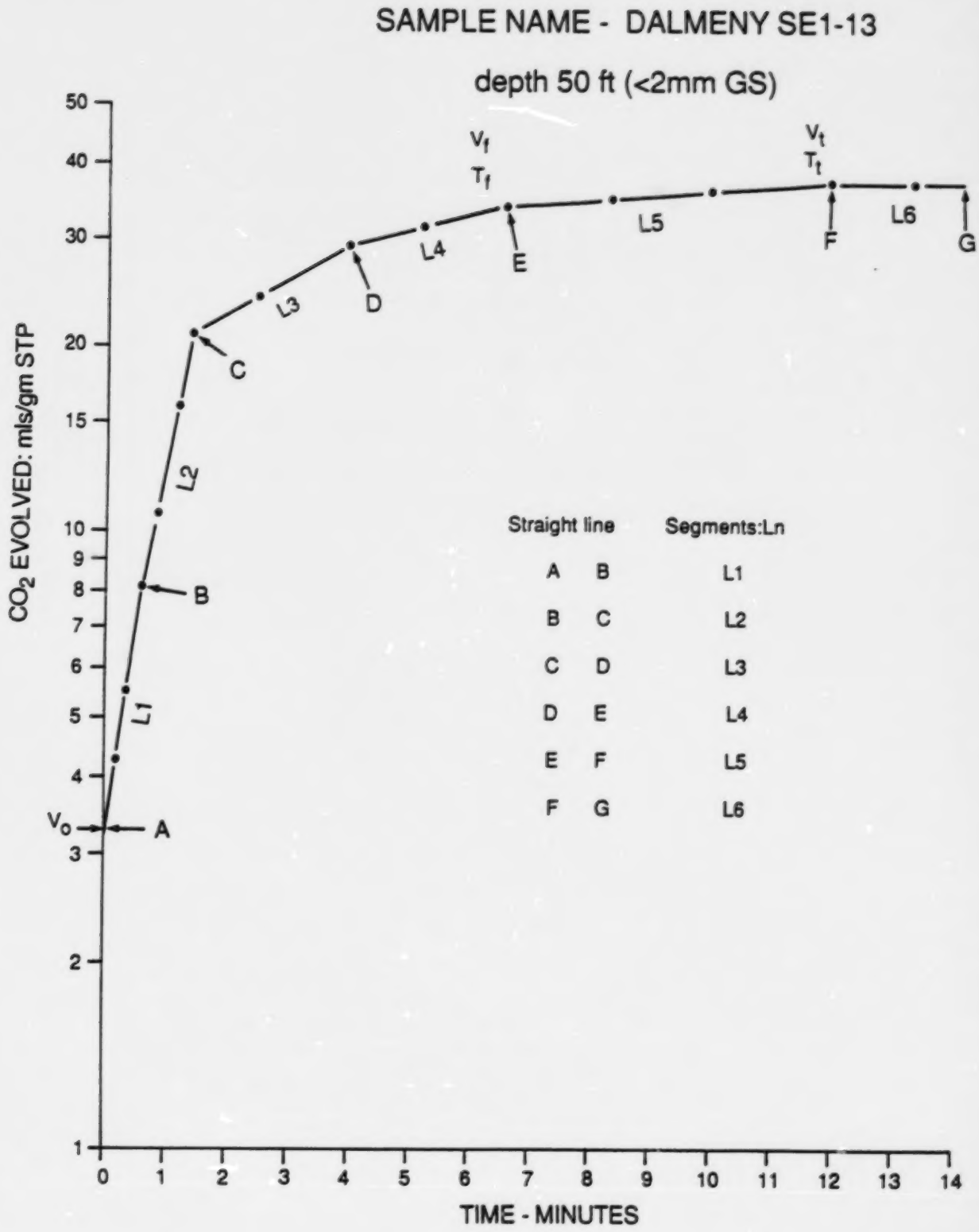


Figure 3B. Semi–Log Graph: Parameter Locations

Figure 4. Record of Data from Gasometer Analysis.

Analytical Record of Data: Carbonate Analysis by Heinze Gasometer Method

Sample Name – Dalmeny SE1–13: 50 ft.; Rotary cuttings

Location – Saskatoon, 73B/2

Submitted by – B.T. Schreiner Sample Treatment: Std.

Analyzed by – W.C. Ross

Date of Analysis – April 4, 1986

Sample weight – 1.00 gm.; Grain Size – < 2.00 mm.

CO_2 volumes (mls) and time (min.)

V_1 – 37.0 mls.; t_1 – 12.0 min.

V_f – 33.8 mls.; t_f – 6.6 min.

V_o – 3.3 mls.; t_o – 0 + t min.

$D_c = V_1 \times \frac{t_f}{t_1} = 20.35$ mls (mls off with calcite)

$V_c = \frac{V_f + V_o - D_c}{2} = 8.38$ mls (CO_2 evolved by calcite)

$V_d = (V_1 - V_c) = 28.62$ mls (CO_2 evolved by dolomite)

Weight Percentages:

Calcite = 3.7% (V_c x .44683) (by AA–3.7)

Dolomite = 8.38% (V_d x .41163) (by AA–11.7)

Total CO_2 Evolved = 36.8 mls (STP – 0°C and 760 mm.Hg) (by AA–36.8)

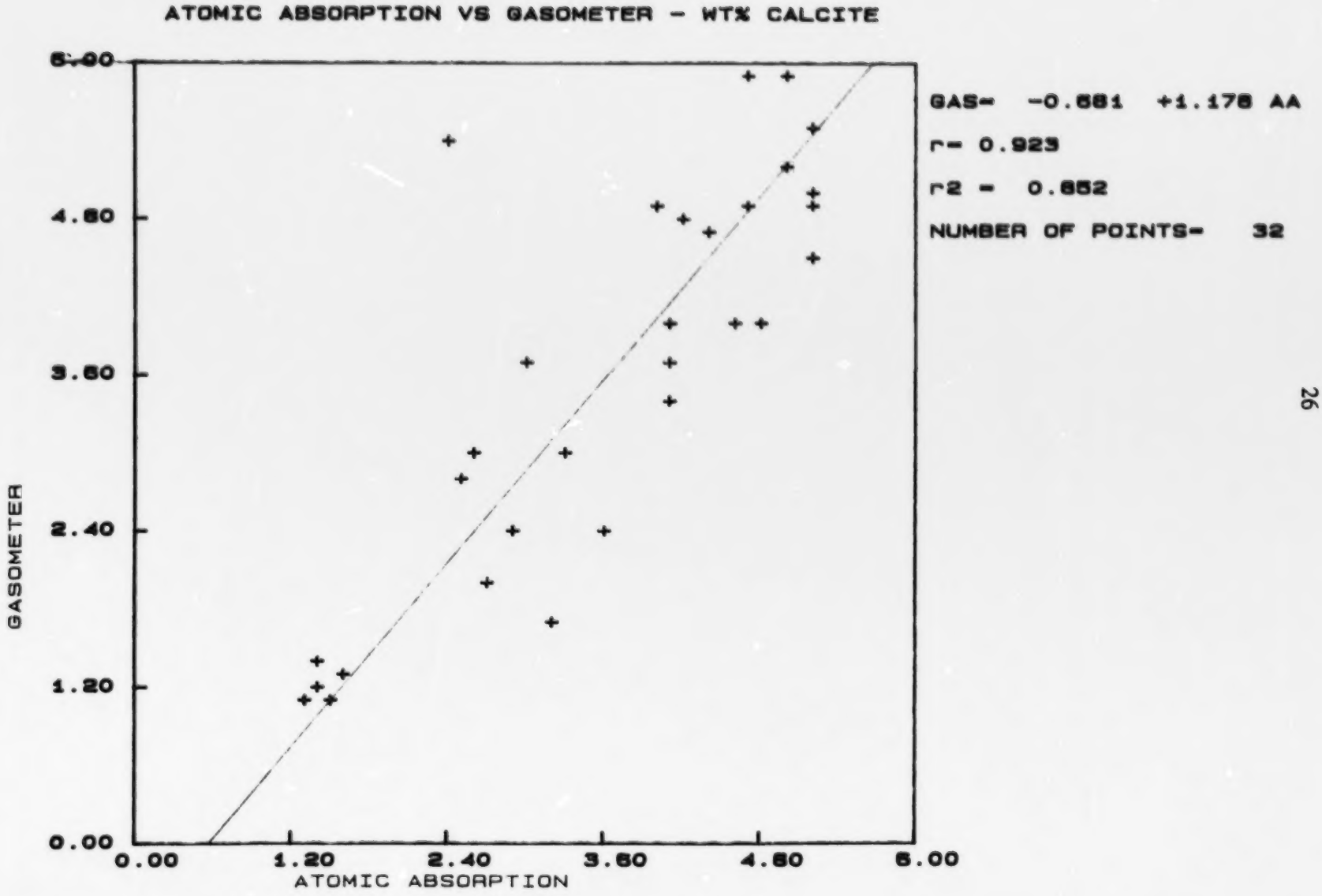


Figure 5 - Linear Regression for Weight Percent Calcite.

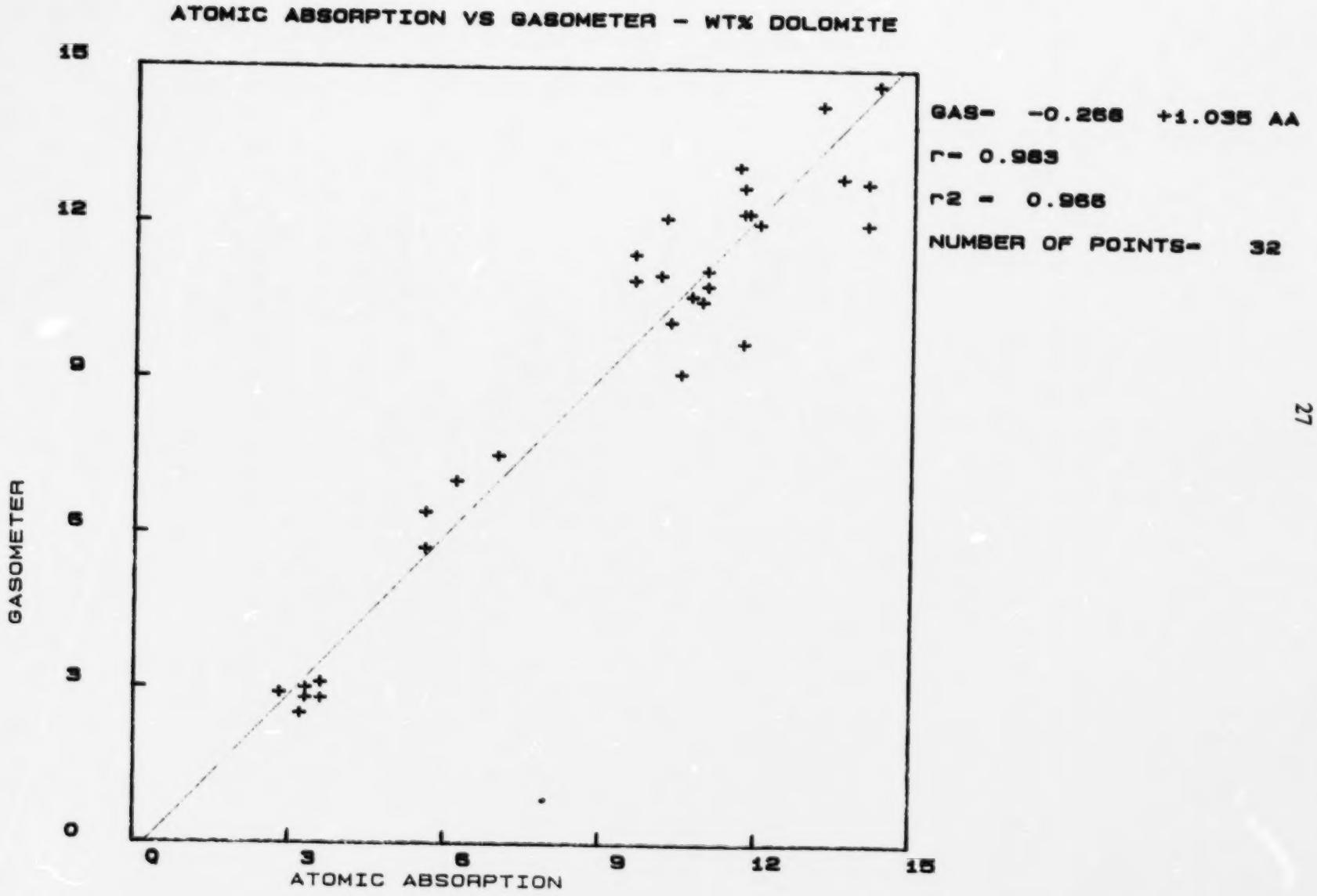


Figure 6 - Linear Regression for Weight Percent Dolomite.

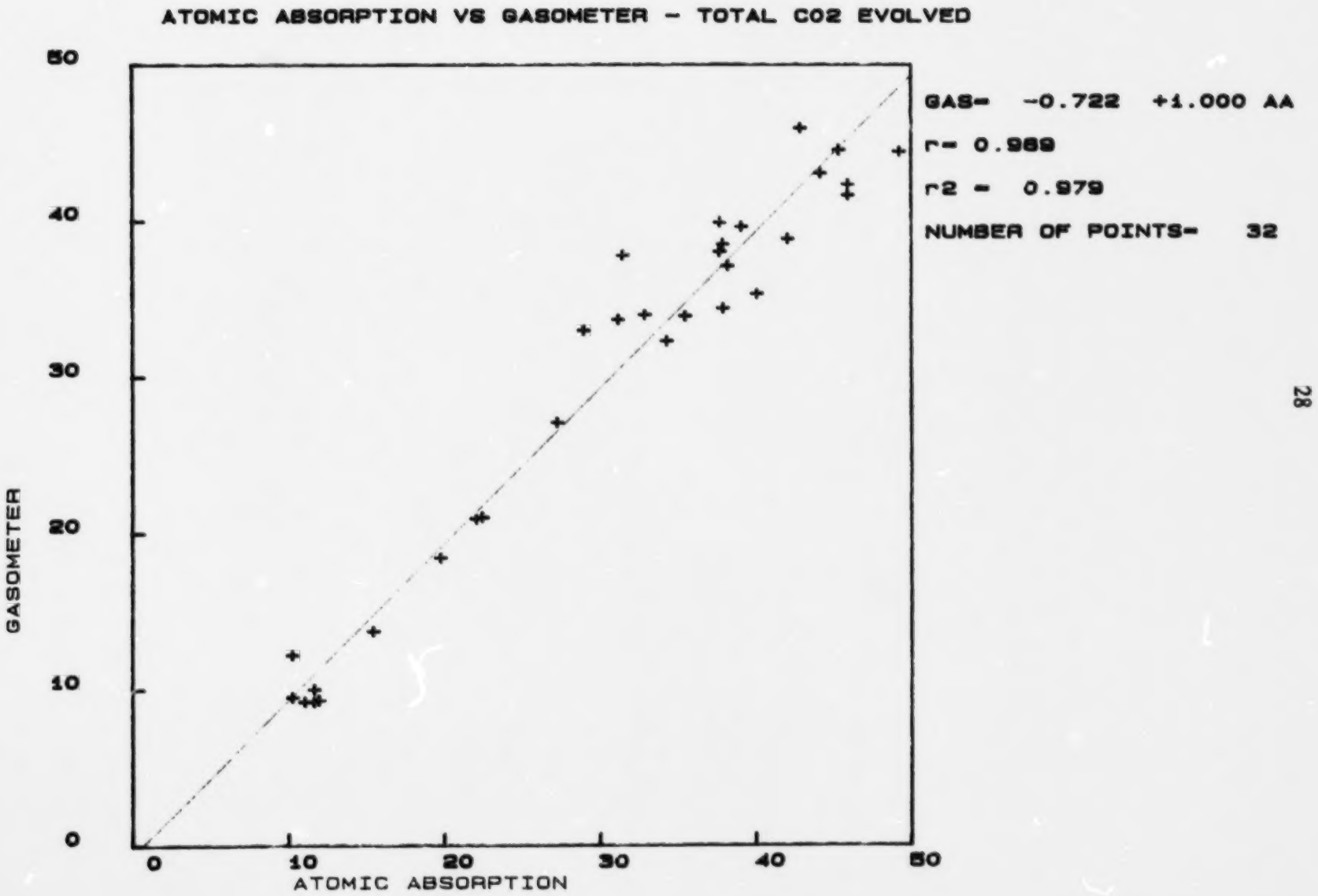


Figure 7 - Linear Regression for Total CO_2 Evolved: $m/s_{/am}$

APPENDIX

FORM OF LABORATORY MANUAL

APPENDICES: LABORATORY OPERATIONS FOR CARBONATE ANALYSES BY THE HEINZE GASOMETER METHOD

APPENDIX 1A. Sample Preparation

PHASE 1 (< 2 mm fraction)

(1) Ovendry samples for 5 hours at a control temperature of 105°C, then cool in desiccator.

(2) Reduce clods, or aggregates, with a wooden rolling pin on a wooden board.

(3) Sieve each sample through a 2 mm screen. Pebbles retained on screen are discarded, or bottled and labelled for future mineralogic studies.

(4) Transfer minus 2 mm screenings into a pre–labelled glass bottle and reheat in drying oven at 105°C for 1 1/2 hours.

(5) Cool samples in a desiccator.

(6) Remove samples and cap bottles.

NOTE: These samples may be placed in reserve for gasometer analyses. This < 2 mm fraction requires longer gasometer time for analyses. To ensure more complete mixing it is advisable to treat samples as outlined by PHASE 2.

PHASE 2 (< 0.0625 mm)

(7) Samples are then reduced by mechanical grinding in a Seimans Cylindrical grinder for six minutes (Christiansen and Ross, 1971).

(8) Collect samples in pre–labelled glass bottles.

(9) Reheat in drying oven at 105°C for 1 1/2 hours.

(10) Cool in desiccator.

(11) Recap and place samples in reserve for gasometer analyses.

APPENDIX 1B. Gasometer Adjustments

NOTE: The gasometer is adjusted to read volumes of CO_2 gas in mls. per gram of sample at standard temperature and pressure, i.e. 0°C and 760 mm Hg. A weighed sample of std. calcium carbonate is dissolved by HCl to evolve CO_2. The CO_2 volume must be within the working range of the gasometer. It was determined that 0.3000 gm of the standard calcium carbonate evolves 67.2 mls of CO_2, at STP, and that this eight per gram of sample is near the maximum weight for free calcite that is dispersed within the tills of southern Saskatchewan.

The Heinze Gasometer adjustment is a volume adjustment which is made to the gas chamber. This is done by the plunger appendage. The other adjustments are made on the (electronic) print–out recorder which is as follows:

Heath – Schlumberger, one point

Model – SR204

The preliminary adjustments, are as follows:

(1) Turn switches to 'on' position (i.e. control panel and recorder). Warm up electronics for 5 minutes.

(2) Stirrer off, on 10V scale[1], record pen position as P1 mls.

(3) Stirrer off, on 10V scale[1], analyse 0.30000 gm of Standard Calcite (ACS), record pen position as P2.

(4) Stirrer off, on 10V scale[1], adjust gasometer plunger so that volume of P2 – P1 = 45.7 mls.

(5) Stirrer off, on variable scale[1], with recorder adjusting screw, adjust pen to read 67.3 mls.

(6) Stirrer off, open system, with zero adjusting knob, adjust pen to read 0.0 mls.

(7) Stirrer on, close system, sample and acid in place, adjust pen to 0 mls, open acid valve.

(8) Recorded volumes are mls CO_2 per gram of sample, at STP.

APPENDIX 1C. Laboratory Analysis

Preliminary: Allow electrical components to stabilize:

(1) Set main power switch of electrical control panel to 'on' position. Turn recorder power switch to 'on' position. Allow electrical components to warm up for 10 minutes.

Adjust volumes to read Standard Temperature and Pressure (STP)

(2) Weigh 0.3000 gm of standard ACS calcium carbonate.

(3) Transfer standard sample to gasometer flask. Add magnetic stirrer.

(4) Add exactly 20.0 mls of 1:1 HCl acid to acid–dispenser from calibrated syringe.

(5) Place gasometer flask and sample in sample rack.

(6) Close gasometer system with acid cock closed.

(7) Set recorder adjustment dials – chart speed switch to 1 cm/min., advance functional switch to chart position. Turn switches to 'on' position for acid dispenser and magnetic stirrer.

(8) When the CO_2 evolution curve traced on recorder–chart shows final volume (curve flattens) then analysis is finished. If necessary, adjust final volume to read 67.2 mls, Ref. Appendix 1B,step 5.

(9) Open gasometer system. Clean acid off flask retaining ring.

NOTE: During a sample analysis the recorder prints a continuous CO_2 evolution curve which is traced on arithmetic graph paper. (Example – Figure 2A – Arithmetic Graph).

(10) Add exactly 20.0 mls of 1:1 HCl acid to acid–dispenser from calibrated syringe.

(11) Set functional switch of recorder at pen position.

(12) Add exactly 1.0000 gm of sample to gasometer flask, add magnetic stirrer.

(13) Close gasometer system.

(14) Zero recorder pen. Ref. – Appendix 1B, step 3.

(15) Advance functional switch to chart position. Simultaneously turn acid dispenser and magnetic stirrer switch to 'on' position.

(16) When CO_2 evolution curve of recorder chart shows final volume then analysis is complete.

NOTE: Volumes are STP, and units are mls of CO_2 per gram of sample.

For continuous carbonate analyses, repeat steps (9) to (16) for each sample.

Every four hours of continuous operation, it is advisable to verify that the recorded volumes are STP. Analyse and standard calcium carbonate sample, and, if required, make the necessary gasometer adjustments that are described in Appendix 1C, steps (2) to (8).

APPENDIX 1D: Interpretation of CO_2 Curves

(1) Set up model for interpretation:

Replot the (recorder print–out) Arithmetic Graph to the (2 cycle semilogarithmic) Semilog Graph. The semilog graph is used for the interpretation of the required parameters which are used for the calculations of the gas volumes from calcite and dolomite.

Follow general rule to pick the graph parameters, as follows:

V_t – total volume of evolved CO_2 (from calcite and dolomite)

– the last straight–line segment parallels time axis. Read this volume and record, unit is mls.

With reference to Figure 3B, this is at point F, V_t = 37.0 mls.

t_t – time that V_t is reached. This is also total time of reaction.

With reference to Figure 3B, this is at point F, the intersection of segments l_5 and l_6.

It is the time at the intersection of the last two straight line segments. Read and record in minutes.

V_f – total volume of CO_2 evolved from calcite

– Read volume at intersection of second and third last segments.

The second last segment is the rate of CO_2 evolution from dolomite only, based on rule, rate of CO_2 evolution from calcite is greater than the rate of CO_2 evolution from dolomite.

With reference to Figure 3B, segment l_5 is CO_2 from dolomite only, V_f is at point E, the intersection of segments l_4 and l_5. V_f = 33.8 mls. Read this volume and record.

t_t – This is the time of completion for total CO_2 evolution from calcite. It is the time at the intersection of the second and third last segment. With reference to Figure 3B it is intersection of l_4 and l_5. V_t = 5.8 minutes. Read and record.

V_o – is the apparent volume at time of zero minutes.

– It is the intersection of the first segment with the volume axis at time zero minutes.

With reference to Figure 3B, it is the volume by the intercept of segment l_1 with the volume axis. V_o = 3.2 mls. Read and record.

Calculations of Intermediate Parameters

D_c – is volume of CO_2 from dolomite which is evolved with total calcite CO_2.

$D_c = V_t \times \frac{t_t}{\overline{t_t}}$ mls, calculate and record in record sheet, Figure 4.

V_c – is the total CO_2 evolved by calcite.

$V_c = \frac{V_t + V_o - D_c}{2}$ mls

V_d – is total CO_2 evolved by dolomite.

$V_d = V_t - V_c$ mls.

APPENDIX 1E – Calculations for Calcite and Dolomite

The weight percentage of each carbonate mineral, calcite and dolo mite, is calculated by using stoichiometric relationships of the chemical reaction of HCl with each respective mineral.

Calculations are as follows:

Calcite –

$$\text{Wt \% Calcite} = \frac{\text{Volume of Calcite (STP)} \times \text{Gram Equiv. Wt. } CaCO_3 \times 100}{\text{m.w. } CO_2 \times 1.00}$$

$$\text{Wt \% Calcite} = V_c \times 0.44683$$

Dolomite –

$$\text{Wt \% dolomite} = \frac{\text{Volume of Dolomite (STP)} \times \text{Gram Eq.wt. } CaMg(CO_3)_2 \times 100}{\text{m.w. } CO_2 \times 100}$$

(assumption – Ca:Mg = 1:1)

$$\text{Wt \% dolomite} = V_d \times 0.41163$$

NOTE: Both the graphic and calculated parameters are recorded in an orderly fashion for future reference, Figure 4 is an analytical data sheet which is used by the laboratory for permanent records.

APPENDIX 1F: Analytical Record of Data: Carbonate Analysis by Heinze Gasometer Method

Sample Name –

Location –

Submitted by –

Analyzed by –

Date of Analysis –

Sample weight – gm.; Grain Size – < mm.

CO_2 volumes (mls) and time (min.)

V_1 – mls.; t_1 – min.

V_f – mls.; t_f – min.

V_o – mls.; t_o – 0 + t min.

D_c – $\frac{V_1 \times t_f}{t_1}$ = mls (mls off with calcite)

$V_c = \frac{V_f + V_o - D_c}{2}$ = mls (CO_2 evolved by calcite)

$V_d = (V_1 - V_c)$ = mls (CO_2 evolved by dolomite)

Weight Percentages:

Calcite = % (V_c x .44683)

Dolomite = % (V_d x .41163)

Total CO_2 Evolved = mls (STP – 0°C and 760 mm.Hg)